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# **“La tutela dell’Ambiente e dei Beni Culturali in un Mondo che cambia”**

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## Identification of the lichen species in historical orchil dyes by HPLC-MS: a preliminary study

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### 1. Introduction

Orchil is a purple dye extracted from lichens, widely used since 6<sup>th</sup> century [1] as a substitute for the rare and expensive *Tyrian purple*. It was used for dyeing parchments, yarns and textiles and as a colourant in illuminated manuscripts. The dye was produced since Antiquity by soaking lichens in ammonia in order to promote the transformation of the chemical precursors. The process is slow, as it takes at least three weeks, and produces phenoxazonic compounds collectively known as orceins[2].

Orchil can be obtained from different lichen species, which are native of specific regions or geographical areas. Since each species can have a typical set of chemical precursors, the final set of orceins could be characteristic of the species, even if the macroscopic features of the dye could be similar in terms of hue and spectral responses upon analysis. The goal of our project is identifying a recognition pattern of the most common lichen species (*Lasallia pustulata*, *Ochrolechia tartarea*, *Roccella tinctoria*) by means of HPLC-MS analysis, in order to develop a tool linked geographical specificity, useful to determine the origin of real samples dyed with orchil. This information could in fact lead to hypothesise the possible trade and exchange routes of the purple dye.

Through the creation of a database obtained from the analysis of three standards extracted from lichens, prepared in the laboratory using ancient recipes, and a synthetic standard (orcein, Sigma-Aldrich), we have studied the composition of some wool and silk fabrics dyed with orchil of known species by expert craftsmen, and of four real samples (Fig.1) with different origins and dates: (a) a fragment of purple parchment from the *Codex Brixianus*, a purple codex (6<sup>th</sup> century, Biblioteca Civica Queriniana, Brescia); (b) a wool fragment of the embroidery on the cover of the *Medical Almanac MS.8932* (1420, Wellcome Library, London); (c) a silk thread taken from a charter of the *Privilegium maius*, a fraudulent document created by Habsburg Duke Rudolf IV (1358-1359, Österreichisches Staatsarchiv, Vienna); (d) a fragment of purple parchment from the *Vienna Genesis*, a purple illuminated manuscript (6<sup>th</sup> century, Österreichische Nationalbibliothek, Vienna).

### 2. Results and Discussion

*Lasallia pustulata*, *Ochrolechia tartarea* and *Roccella tinctoria* were chosen because they can be reputed as the species more commonly used in the past [3]. The orchils obtained from the three lichen species studied in this work showed a slightly different composition compared to that of their synthetic version, i.e. Sigma-Aldrich's orcein, and also showed some specific components for each species. Through the use of this diagnostic method, combined with a multivariate analysis using the principal component method (PCA), it was possible to discriminate the three groups (items dyed with *Lasallia pustulata*, with *Ochrolechia tartarea* and with *Roccella tinctoria*) and, on this base, to determine the lichen species used for the different real samples, as well as hypothesising their geographical origin area or the commercial route through which orchil was sold in the past.



**Fig. 1** – a) *Codex Brixianus* (6<sup>th</sup> century, *Biblioteca Civica Queriniana*, *Brescia*), b) *Privilegium maius*, charter AUR 1845 (1358-1359, *Österreichisches Staatsarchiv*, *Vienna*), c) *MS.8932* (1420, *Wellcome Library*, *London*), d) *Vienna Genesis* (6<sup>th</sup> century, *Österreichische Nationalbibliothek*, *Vienna*)

### 3. Conclusions

Orchil is one of the most used purple dyes in the ancient world, although it has been rarely identified by chemical analysis; in addition, there are very few studies are focused on the possible identification of the lichen species used [4]. The present study provides preliminary results towards the development of a useful method for the recognition of three of the most widespread lichen species used to obtain orchil, applied to the characterization of the dye when used for dyeing purposes of fabrics, yarns and parchments. Of course the use of further lichen species for the production of orchil in Antiquity and in middle Ages cannot exclude, and further work is necessary in order to consider all the possible sources. .

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